

MONSANTO RESEARCH CORPORATION

BOSTON LABORATORY · EVERETT, MASSACHUSETTS 02149

26 June 1967

DUNKIRK 9-0480

Chief, Solar and Chemical Power Systems - Code RNW
NASA Headquarters
Washington, D. C. 20546

Ref: Contract NASW-1527
Quarterly Report No. 1

Gentlemen:

Enclosed is the subject report. Please acknowledge receipt of the report by signing and returning the enclosed post card.

Copies of this report have been distributed in accordance with the list included as the final page of the report.

Very truly yours,

T. G. Linxweiler
Technical Editor

TGL/jf
Enclosures

FACILITY FORM #02	N 67-37084	
	(ACCESSION NUMBER)	(THRU)
	12	1
	(PAGES)	(CODE)
	CP#88547	06
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

MRB5012Q1

Quarterly Report No. 1
TEST EVALUATION OF FUEL CELL CATALYSTS
15 February to 15 May 1967

Contract NASW-1527

20 June 1967

For

NASA Headquarters
Washington, D.C. 20546

Prepared by

R. F. Drake
S. Matsuda
B. P. Sullivan

MONSANTO RESEARCH CORPORATION
BOSTON LABORATORY
Everett, Massachusetts 02149

TABLE OF CONTENTS

	<u>Page</u>
I. SUMMARY	1
II. INTRODUCTION	2
III. PREPARATION OF CATALYSTS	3
IV. ELECTRODE PREPARATION	4
V. TEST RESULTS	5
A. WITH DEXTROSE	5
B. N_2H_4 OXIDATION	5
VI. FUTURE WORK	7

I. SUMMARY

During the first quarter of the contract, the first group of compounds supplied by the U. S. Bureau of Mines was tested for catalytic activity in the oxidation of dextrose and N_2H_4 .

These compounds were interstitial compounds of iron.

Results indicated that no compounds were catalytically active for dextrose oxidation in buffered neutral electrolyte, but all compounds were sufficiently active for N_2H_4 oxidation in KOH electrolyte. Some compounds, particularly those prepared from leached Raney iron, however, showed significantly severe corrosion in the caustic electrolyte.

II. INTRODUCTION

Advancements in fuel cell technology during the last decade showed promise for the use of fuel cells as a continuously operable power source, both in space and on ground.

One of the most critical problems associated with the further development of the fuel cell, particularly for their more common applications, is undoubtedly the development of high efficiency, low cost (non-noble metal) catalysts. Difficulties involved in this task include the high complexity of electrocatalysis, which none of the existing mechanisms and theories on the heterogeneous catalysis can directly explain, and problems in preparing equivalent catalysts from non-noble metal compounds.

The availability of various promising interstitial compounds, borides, nitrides, carbides and carbonitrides with favorable physical properties, synthesized by the Bureau of Mines, offered us a delightful opportunity to investigate the electrocatalytic activity of these compounds for oxidation of various fuels, at Monsanto Research Corporation under Contract NASW-1527.

The experimental program undertaken at MRC includes the determination of certain essential properties, such as electrode polarization characteristics and corrosion resistance to neutral and caustic electrolytes.

III. PREPARATION OF CATALYSTS

Since these catalysts were pyrophoric in nature and were shipped out in small bottles encapsulated under an inert gas atmosphere, preconditioning was necessary before complete exposure to air.

All capsules were placed in a dry box, then carefully opened after the air in the box had been thoroughly replaced by chemically pure argon. A small amount of air (corresponding to less than 1%) was then mixed into the argon stream. After a sufficient time for stabilization, air was very gradually increased to the atmospheric level. This process took several hours.

Since some of the catalysts were too coarse for the MRC electrode manufacturing method* they were ground and sieved to -44 mesh particles. Although it is desirable to grind in an inert atmosphere, the grinding was actually carried out in air and resulted in a loss of one catalyst (Sample 18N) by ignition.

* Proprietary method of Monsanto Research Corporation

IV. ELECTRODE PREPARATION

For the electrode evaluation tests, two types of electrode structures were used. The methods for preparing both types are Monsanto Research proprietary. Properties of the two electrodes are essentially similar. Both are microporous electrodes consisting of catalyst particles and bonding agent particles, supported on a current collector metal screen. Differences between the two electrodes include: (1) Type AC (MRC) has higher material density than Type B (MRS), (2) Type A is a uniform micro-porous structure, while Type B contains a network of macropores in a micro-porous matrix, and (3) Type A is more hydrophobic than Type B. Therefore, it was expected that Type B was more suitable to the present project in which test fuels are dissolved in (2) the aqueous electrolyte.

V. TEST RESULTS

A. WITH DEXTROSE

Compounds for the anodic oxidation of glucose were evaluated for catalytic activity under contract PH43-66-976 of the National Heart Institute, Department of Health, Education and Welfare.

The test electrolyte was an aqueous solution of 0.5 M NaCl, 1 M phosphate buffer (pH 7.4) and 0.5 M dextrose. Temperature of the electrolyte was maintained at 37°C.

1 x 1 inch electrodes of Type B (MRS) were used for the tests. After determining the steady state open circuit potential in the deaerated electrolyte (N₂ bubbling for a sufficient time for deaeration), the potential-time curve was determined at the anodic current density of 1 ma/cm².

All electrodes tested to date took 30 minutes to one hour to reach steady state open circuit potential. The open circuit potentials were somewhat different from one catalyst to another, approximately 0.2 to 0.4 volt less than the reversible hydrogen electrode in the same electrolyte, whereas active catalysts such as precious metals or some chelates in the same electrolyte commonly indicates the open circuit potentials very close to the hydrogen electrode potential.

By passing the anodic current, the potentials of all electrodes then showed practically an instantaneous anodic polarization of 0.5 volt or more, indicating that the catalysts tested do not bear any significant activities for the oxidation of dextrose.

One electrode (19N- ζ -Fe₂N, ϵ -Fe₃N) seemed slightly active since it sustained a relatively active potential when the current was passed. However, chemical analysis of the electrolyte proved that the current had actually been used to dissolve the catalyst.

B. N₂H₄ OXIDATION

Tests for catalytic activity of the compounds for the anodic oxidation of N₂H₄ were carried out under contract DA28-043-AMC-01996(E) of the United States Army Electronics Command, Fort Monmouth, New Jersey.

The test electrolyte was 5M KOH combined with 2M N₂H₄. All electrodes were tested at 70°C. Some were also tested at 30 and 50°C. These compounds could be corroded, to some extent, in a strong caustic solution, such as the test electrolyte. However,

it was hoped that presence of very active fuel and a strong reducing agent, might prevent the corrosion. Electrodes of both Type A and B were used for the tests. After determining the steady state open circuit potential in the electrolyte, the anodic polarization curve was made galvanostatically by increasing the current from 1 to 100 ma/cm², step wise. Each step of the current was kept for a sufficient time, so that the electrode reached a nearly steady state at each level.

During the tests, corrosion of some catalysts was readily noticed. All compounds prepared from leached Raney iron were particularly corrosive. Among the electrodes made from these compounds, some electrodes quickly decomposed, even before any current was passed. The others first swelled up, then gradually separated from the platinum current collector screen and finally fell into pieces. The corrosion was also confirmed by chemical analysis of the electrolyte after the tests. The interesting fact was that despite the significant corrosion, the potentials of these electrodes, when measurable, were that of the hydrazine electrode, suggesting that they were catalytically active.

The compounds prepared from an alkali-promoted magnetite and from coprecipitated oxides of Fe and Ag showed very little or no corrosion and were catalytically active.

IR drop through the electrode and a short path of the electrolyte between a Lugin capillary and the electrode surface was determined by using the Kordes-Marko bridge. Results suggest that all compounds tested have reasonably high electrical conductivities. Polarization data of the useful range in the fuel cell practice are given as IR free electrode potentials vs the saturated Calomel electrode at various current densities above 10 ma/cm² (apparent densities) in Table I in the Appendix.

VI. FUTURE WORK

During the second quarter, the second group of compounds, which are mainly interstitial compounds of non-ferrous metals, will be tested.

Based on the results of our work in quarter 1, only Type B electrodes will be used for this study.

Table 1
POTENTIAL OF VARIOUS N_2H_4 ELECTRODE
VS. THE SATURATED CALOMEL ELECTRODE
AT VARIOUS CURRENT DENSITIES (IR FREE)

ELECTROLYTE: 5M KOH + 2M N_2H_4

Catalysts	Electrode Type	Temp.	OCP	Current Density, ma/cm ²			
				10	20	50	100
10C: θ -Fe ₃ C, α -Fe	A	70	-1.13	-1.13	-1.10	-1.09	-1.03
	B	70	-1.18	-1.18	-1.17	-1.13	-1.08
11C: χ -Fe ₂ C	A	70	-1.15	-1.15	-1.14	-1.13	-1.11
14C: θ -Fe ₃ C	A	70	-1.13	-1.13	-1.11	-1.08	-1.01
1N: ϵ -Fe ₃ N, γ' -Fe ₄ N	A	70	-1.16	-1.15	-1.13	-1.11	-1.07
6N: ϵ -Fe ₃ N, ζ -Fe ₂ N	A	70	Electrode decomposed				
9N: ζ -Fe ₂ N	A	70	-1.17	-1.16	-1.15	-1.13	-1.12
10N: ϵ -Fe ₃ N	A	70	-1.20	-1.17	-1.16	-1.05	-0.97
	A	50	-1.16	-1.15	-1.13	-1.08	-0.97
	A	30	-0.92	-0.78	-0.74	-0.68	-0.62
	B	50	-1.20	-1.15	-1.13	-1.11	-1.07
19N: ζ -Fe ₂ N, ϵ -Fe ₃ N	A	70	-1.21	-1.19	-1.16	-1.10	-1.05
	A	50	-1.20	-1.19	-1.16	-1.10	-1.08
	A	30	-1.13	-1.11	-1.11	-1.04	-0.92
	B	50	-1.20	-1.17	-1.15	-1.11	-1.06
21N: γ' -Fe ₄ N, ϵ -Fe ₃ N	A	70	-1.22	-1.21	-1.20	-1.19	-1.12
	A	50	-1.02	-1.07	-1.13	-1.12	-1.10
	A	30	-0.86	-0.76	-0.70	-0.62	-0.55
	B	50	-1.22	-1.17	-1.17	-1.15	-1.15
2NC: χ -Fe ₂ X(C,N), ϵ -Fe ₂ X(C,N)	A	70	-1.18	-1.17	-1.16	-1.16	-1.15
	A	50	-1.17	-1.17	-1.16	-1.13	-1.12
	A	30	-1.16	-1.15	-1.09	-1.07	-1.03
	B	70	-1.18	-1.19	-1.18	-1.17	-1.14
3NC: ϵ -Fe ₂ X(C,N)	A	70	-1.19	-1.19	-1.18	-1.15	-1.12
	A	50	-1.14	-1.15	-1.14	-1.11	-1.07
	A	30	-1.03	-1.07	-1.03	-0.99	-0.99
	B	50	-1.20	-1.08	-1.05	-0.96	-0.86
5NC: θ -Fe ₃ X(C,N)	A	70	-1.15	-1.13	-1.13	-1.10	-1.10
1CN: ϵ -Fe ₂ X(C,N)	A	70	-1.19	-1.19	-1.18	-1.15	-1.12
	A	50	-1.15	-1.15	-1.15	-1.14	-1.12
	A	30	-0.86	-0.65	-0.58	-0.47	-0.33
2CN: ϵ -Fe ₂ X(C,N)	A	70	-1.10	-1.10	-1.09	-1.07	-1.03
5CN: ϵ -Fe ₂ X(C,N)	A	70	-1.10	-1.11	-1.10	-1.08	-1.05
9CN: γ' -Fe ₄ X(C,N)	A	70	-1.19	-1.16	-1.14	-1.14	-1.10
	A	50	-1.14	-1.18	-1.16	-1.14	-0.98
	A	30	-0.99	-0.96	-0.78	-0.64	-0.60
	B	50	-1.22	-1.15	-1.13	-1.10	-1.07

DISTRIBUTION LIST

Chief, Solar & Chemical Power Systems
Code RNW
NASA Headquarters
Washington, D.C. 20546 (8)

New Technology Representative
Office of Technology Utilization - Code UT
NASA Headquarters
Washington, D.C. 20546

Scientific and Technical Information Facilities
P. O. Box 33
College Park, Maryland 20740

Attention: NASA Representative

Ernst M. Cohn
Code RNW
NASA Headquarters
Washington, D.C. 20546

Dr. Eugene Weissman
General Electric Research Laboratory
P. O. Box 1088
Schenectady, New York 11500

Mr. D. Bienstock
Bureau of Mines
4800 Forbes Avenue
Pittsburgh, Pa. 15213

Dr. Seigo Matsuda
Monsanto Research Corporation
1101 17th St., N.W.
Washington, D.C. 20036

Dr. A. Makrides
TYCO Laboratories
Bear Hill
Waltham, Mass. 02154

Dr. George E. Evans
Union Carbide Corporation
Electronics Division
P. O. Box 6116
Cleveland, Ohio 44101

Dr. D. Pouli
Allis-Chalmers Mfg. Co.
1100 S. 70th St.
Milwaukee, Wisconsin 53214

Dr. H. J. Goldsmith
Catalyst Research Corporation
6101 Falls Road
Baltimore, Maryland 21209

Dr. C. E. Heath
Esso Research & Engineering Co.
P. O. Box 8
Linden, New Jersey 07036

Mr. Robert J. Flannery
910 South Michigan Avenue
Chicago 80, Illinois